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Spray pyrolytic deposition of ZnO thin layers composed of low dimensional nanostructures

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Abstract

ZnO nanolayers composed of fine nanostructures have been successively grown by spray pyrolytic deposition at 300 °C over amorphous glass substrates. As deposited samples were analysed by scanning electron microscopy (SEM), showing a granular morphology with grain size in the limit of the microscope resolution. CL measurement shows a broad near band edge (3.4 eV) emission of ZnO in the UV region and the defect level emissions in the green region of the spectrum. The use of intermittent spray pyrolytic deposition is shown as an alternative to increase the homogeneity of the samples when temperatures near to the precursor pyrolytic decomposition is selected, long depositions times are involved, and low thermal conductive substrates are used. We have focused on one of these low thermal conductive substrates, glass, on which spheroid shaped microstructures and inhomogeneities appear.

Keywords: ZnO nanolayers, Nanostructures, SEM, Cathodoluminiscence.

1. Introduction

ZnO is a wide band gap (3.37 eV) transparent semiconductor having potential applications in the field of solar energy harvesting electrodes, LED's, next generation UV sources, micro and nano lasers, flat panel displays, gas sensors, photo catalysis, and biosensors among other [1-6]. ZnO is a non toxic material with high exciton binding energy (60 meV), which should allow to fabricate room temperature light emission sources. ZnO being an oxide material, generally protective layers are not required while using it as a material for device fabrication. Recently, solution based synthesis methods have attained considerable focus as a choice for the synthesis of ZnO micro/nanostructures due to its cost effectiveness [6,7]. Spray pyrolytic thin film deposition method is one of the best techniques due to its instrumentation simplicity, and its suitability for large area deposition in a short span of time as compared to other more expensive methods [3,4]. There is a growing demand for extremely thin nonlinear optical material for pulse characterization, frequency conversion of pulses with ultrashort time duration [4].

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Furthermore, ZnO thin layers composed of nanostructures with dimensions near to the Bohr radius, are expected to exhibit interesting physical and optical properties due to the quantum confinement effect, and their large surface to volume ratio [5, 6]. Within this frame, it is fundamental to know the basics of the growth processes. Here, we present a study of the growth of ZnO nanolayers by using the spray pyrolysis technique, in order to deep in the understanding of the correlation between morphology and the growth conditions, aiming to the fabrication of ZnO nanostructures for new applications, based on both the quantum confinement and the surface effects.

2. Experimental

Precursor solutions for the present studies were prepared by dissolving analytical reagent grade zinc acetate (Sigma Aldrich) in a mixture of ethanol (99%) and deionised water in the ratio of 4:1. Ultrasonically cleaned glass slides were used as substrates for a nominal deposition temperature of 300 ^{o}C. Nitrogen gas at a pressure of 0.5 bar was used as the spraying gas to spray the precursor solution over the substrate by using a specifically designed atomizer. The atomizer position was adjusted in order to get fine and homogeneous droplets distribution over the substrate surface. In some of the experiments a little quantity (20 ml) of ethylediamine was added to increase the solubility of the precursor salt. Experiments were performed with different molar solutions of the precursor salt, and different deposition times. The morphology and energy dispersive X-ray spectroscopy (EDX) of the deposited samples were studied in a field emission scanning electron microscope (FESEM-Hitachi S-4100). Cathodoluminescence (CL) measurements were carried out with a Gatan XiCLone system attached to a scanning electron microscope (Leo 1530/ CarlZeiss) using a CCD detector.

3. Results and discussion

In spray pyrolytic deposition processes, nanolayer thickness, growth orientation, particle size and morphology can be modified by changing the deposition parameters, e.g. the substrate temperature, atomizer to substrate distance, time of deposition, molarity of the precursor solution, spray rate, chemical nature of the precursor salt, etc [2,8,9]. Higher substrate temperatures, as regards the temperature pyrolysis of the precursor, generally favour the growth of large size crystallites. Therefore, the deposition process with a substrate temperature slightly higher than

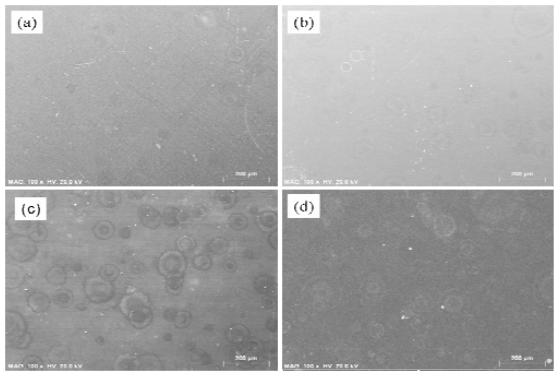

Figure 1. SEM image of spray pyrolytically deposited ZnO nanolayers by using 0.025M precursor solution at a deposition time of (a) 15; (b) 30; (c) 60 and (d) 120 s.

that of the decomposition temperature of the precursor salt can be a good option for the deposition of nanolayers made of ultrafine particles. In our case, we have chosen 300 ºC as a deposition temperature, a little higher than the decomposition temperature of zinc acetate (280 ºC) [3]. Nevertheless, continuous spraying of room temperature (RT) precursor solution over poor thermal conductive substrates, like glass, can generate microdroplets on the substrate surface due to surface tension and low evaporation, and decomposition rate of the precursor solution. This condition eventually leads to the slow evaporation of microdroplets and the formation of thin films composed of a high density of microstructures. Zinc acetate has a good solubility in water and is currently used as a solvent for

spray pyrolytic experiments [9]. But, the evaporation rate of water is low as compared to that of organic solvents like ethanol. In order to enhance the evaporation rate, we have used a solution of water and ethanol, instead of pure ethanol, because of the poor solubility of zinc acetate in ethanol [2]. After performing a systematic study using different ratios of water and ethanol as a solvent of the precursor salt we have determined that an ethanol:water ratio of 4:1 is a good option for fast evaporation and homogeneity of the precursor solution. Molarity of the precursor solution is also an important parameter, which determines the size of the nanostructures in spray pyrolytic deposition. Molarity of the precursor solution of the order of 0.1M or higher will likely produce thin films composed of comparatively large size nanoparticles [9]. Furthermore, the spray rate and quantity of precursor solution sprayed over the substrate surface is also important in determining the morphology and size of the granules forming the film. Spraying of large quantity of precursor solution at a time on the substrate surface will also generate more micro droplets of precursor solution over the substrate surface. By considering the afore said aspects, we performed a spray pyrolytic deposition process at 300 ºC by directing very fine mist of 0.025 and 0.013 M precursor solutions onto the glass substrate.

Scanning electron microscopy (SEM) images of the layers deposited with 0.025 M precursor solution at different deposition times (15, 30, 60 and 120 s) are shown in Figure1. As can be seen, the samples obtained with the lower deposition times show a homogenous aspect with some isolated spheroid shaped microstructures. The population of these spheroids is increased for increasing deposition time. The spheroid shaped microstructures are due to the evaporation and coalescence of microdroplets on the substrate surface. The thermal interaction between the actual heating element, the cooling effect due to the spraying of a room temperature solution, and the low

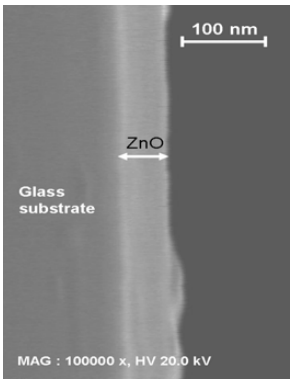

Figure 2. SEM cross sectional view of spray pyrolytically deposited ZnO nanolayers at a deposition time of 60 s by using 0.025 M precursor solution.

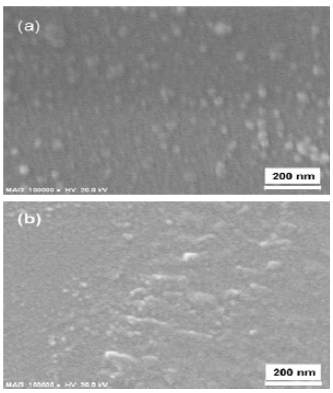

Figure 3. SEM images of spray pyrolytically deposited ZnO nanostructures on glass substrates at a deposition time of 60 s by using (a) 0.025 and (b) 0.013 M precursor solution

thermal conductivity of the substrate, produce an inefficient pyrolytic process and subsequent evaporation. When 0.013 M precursor solution is used with identical experimental conditions the behaviour is very similar. A representative SEM cross sectional image of the sample shows that the layer thickness is of the order of 60 to 90 nm (Figure2). SEM images (Figure 3.) show the presence of fine nanostructures having almost granular morphology especially in the area appearing “bright” in the low magnification SEM images of Fig 1. Most of the granules have sizes less than 20 nm in the limit of the microscope resolution. EDX data confirms the presence of Zn and O in the samples.

The formation of micro droplets irrespective of the molarity with respect to the deposition time is undesirable, especially for depositing layers with higher thickness. The formation of micro droplets and the consequent development of microstructures can be controlled to a certain extent by providing sufficient time to the system for recovering its set temperature. In this case, intermittent spraying with intervals of the order of 2 to 5 minute appears as a good option. We performed experiments with intermittent spraying for longer deposition time, then the micro droplet evaporation points were less than those observed for continuous spraying of the same quantity of material.

The cathodoluminiscence (CL) spectrum shows a broad band with intense contribution at around 385 nm due to near band edge emission (NBE). A broad band luminescence peaking at ≈ 520 nm is also observed in the spectrum (Figure 4).

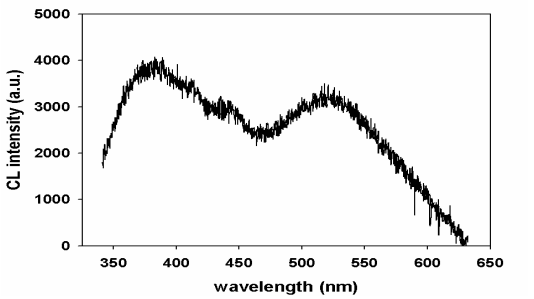

Figure 4. CL spectrum at room temperature of spray pyrolytically deposited ZnO nanostructures at a deposition time of 60 s by using 0.013 M precursor solution added with 20 ml of ethylenediamine.

These two broad emission peaks are generally observed in spray pyrolytically grown ZnO thin films [2]. The broad NBE band, emission intensity is slightly higher than that of the green emission intensity. The broad NBE band, can be attributed to distribution of the nanoparticle sizes. The high energy side of the NBE band suggests the presence of nanoparticles with diameters close to the quantum confinement size limit, which cannot be resolved in the SEM. The green band is usually related to oxygen deficiency [10], therefore, one can assume certain oxygen depletion in these structures.

4. Conclusions

ZnO nanolayers made of low dimensional nanostructures can be effectively synthesized by the spray pyrolysis method by maintaining a low substrate temperature around 300 ^{o}C, and for a short time of deposition. Longer deposition times generate more microstructures and inhomogeneities due to a slow evaporation of the precursor solution, in addition to other effects related with a very inefficient thermal behaviour of the substrate/system, as response to the temperature changes because of the cooling effect of the RT sprayed solution. Providing similar conditions, especially the same temperature for all the impinging fine droplets of the precursor solution onto the substrate surface will generate homogenous ultra thin layers composed of ultra fine particles. The CL spectrum reveals the existence of ZnO, presenting a broad NBE band, probably associated with the existence of nanometer sized hyper fine ZnO particles with varying size distribution, close to the quantum confinement limit.

Acknowledgements

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